

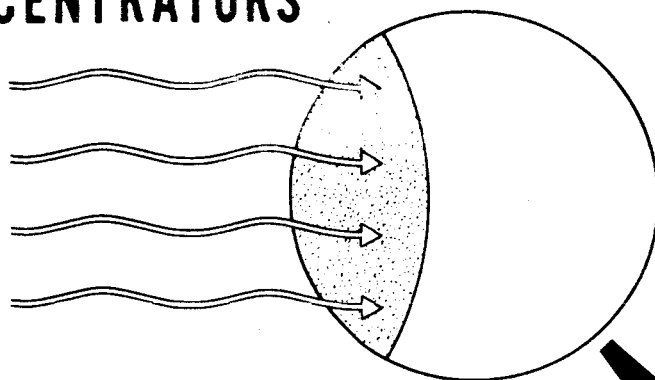
**RIGIDIZED
INFLATABLE
SOLAR ENERGY
CONCENTRATORS**

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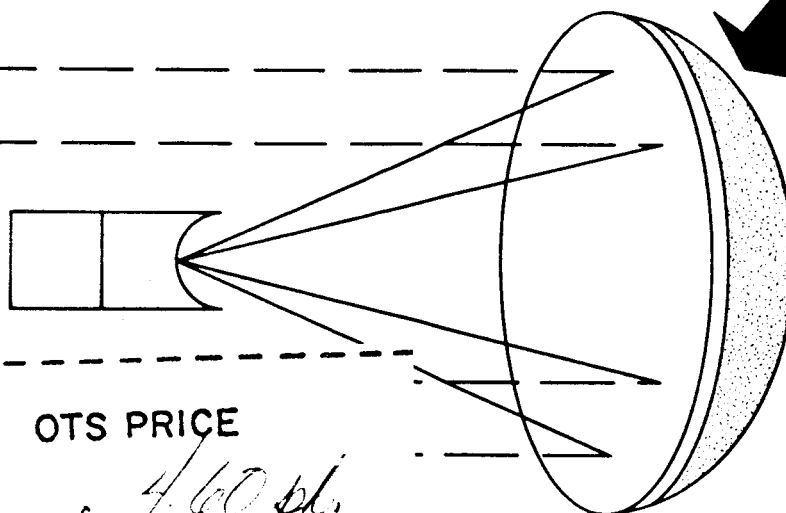
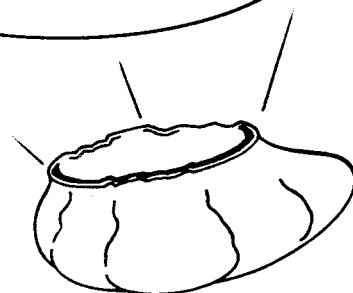
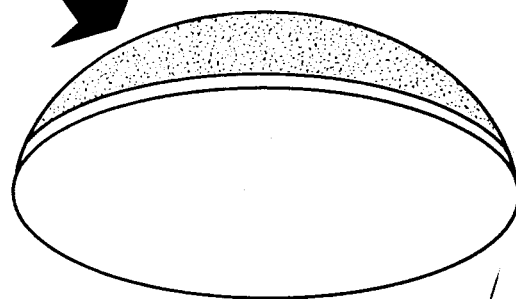
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RIGIDIZED INFLATABLE SOLAR ENERGY CONCENTRATORS

by

N. Jouriles and C. E. Welling

Second Quarterly Progress Report
Covering Period from 1 January through 31 March 1964
Contract No. NAS 1-3301, Control No. L-2923
15 April 1964

Prepared for

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ABSTRACT

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A

This second quarterly progress report covers the work accomplished from 1 January through 31 March 1964. The areas of investigation include (1) chemical and physical property determination of azides, (2) the reduction of heat releases during foaming, (3) sublimation losses during foaming, and (4) the influence of temperature on the foam product. The report analyzes various approaches that were taken during the course of the investigation, and describes the results that were obtained. Detailed data is presented separately in the appendixes.

AUTHOR

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SECTION I. INTRODUCTION

This second quarterly progress report covers the work accomplished from 1 January through 31 March 1964. The major areas of effort include the following:

- (1) Chemical and physical properties of azides.
- (2) The reduction of heat releases during foaming.
- (3) Sublimation losses during foaming.
- (4) The influence of temperature on the foam product.

Chemical and physical property evaluations of available azides were made to determine the extent of azide use in the precoat formulations. Attempts to reduce the heat release involved methods of limiting the percent of azide by prepolymerizing the resin and making use of a blocked isocyanate. Reduction in heat releases have resulted.

Observations were made on volatilization losses of candidate materials upon short time exposure to high vacuum. Studies are continuing to determine sublimation losses during vacuum foaming. Studies of the influence of temperature and compositional variables upon cell structure of foams produced in vacuum have been a continuous effort.

SECTION II. WORK ACCOMPLISHED DURING THIS QUARTER

A. GENERAL

This section outlines the objectives and progress in the various work areas. Experimental detail is given in Appendixes A and B.

B. AZIDE MATERIALS

Evaluation of azide Structures I, X, and XI has been carried to the point that Structure X is rated the most useful of the three. With respect to the various properties desired in an azide, as outlined in the first quarterly progress report (GER 11438), Structure X satisfies several requirements. It is least satisfactory in respect to its heat release (undesirably high) in the Curtius rearrangement to isocyanate and in high melting point and rather low solubility in systems of interest. In view of the general utility of Structure X, larger quantities have been ordered. Since the potential explosive hazards of Structure X have not been fully evaluated, the custom manufacture continues as a repetitive, small-scale laboratory synthesis. The material is received in individual 20-gram packages. Quantities of Structure I have been prepared, as required, in our own laboratory.

A summary of property evaluation results on Structures I, X, and XI is given in Appendix A.

The experimental program in foam development during this quarter has been largely concerned with the heat released by azide rearrangement during foaming.

C. RESIN MATERIALS

The polyol resins first used in precoat formulations and described in GER 11438 are as follows:

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- (1) PFR-6 polyester⁽¹⁾ - a triol with aromatic ring content
- (2) Voranol RS-375 polyether⁽²⁾ - an octol based on sucrose (primary OH)
- (3) HP-370 polyether⁽³⁾ - a tetrol based on methyl glucoside (primary OH)

In order to study less viscous resins and particularly less viscous hydroxyl terminated prepolymers, the following polyether resins are now being used:

- (1) Pluracol TP 440⁽⁴⁾ - a triol
- (2) Pluracol PEP 650⁽⁴⁾ - a tetrol (secondary OH)

Properties of these resins are given in Appendix A. The preparation from these resins of hydroxyl terminated prepolymers with -NCO/-OH reactant ratios varying from 0.24 to 0.75 is also described in Appendix A. Both bulk and solution polymerization techniques have been employed. Toluene diisocyanate (TDI) has been the polyisocyanate reactant. The first attempts to employ 4,4' diphenyl methane diisocyanate (MDI) instead of TDI have encountered some difficulties. However, further work with MDI is planned, because it should contribute more stability against heat distortion than TDI.

The objectives in using prepolymers in precoat formulations are:

- (1) To carry the preliminary build-up of molecular weight of urethane polymer to the point that the system will have suitable viscosity for foaming under the space process condition that foaming gas is liberated at approximately 175°F and higher.

(1) National Aniline Division, General Chemical Co.

(2) Dow Chemical Co.

(3) Corn Products Co.

(4) Wyandotte Chemicals Corp.

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- (2) To limit the amount of isocyanate to be furnished in foaming by azide and thus limit heat release.
- (3) To limit the amount of low molecular weight reactants in the precoat and hence limit possible loss to space vacuum before reaction.

Table I outlines the effect of prepolymering in the case of HP-370 resin; TDI is the isocyanate used in prepolymering.

Table I. Effects of Prepolymerizing

Case	1	2	3
Resin	HP-370 Alone	HP-370 Prepolymered to -NCO/-OH = 0.55	HP-370 Prepolymered to -NCO/-OH = 0.25
Wt % Structure X in precoat for final -NCO/-OH = 1	50.5	25.9	36.3
Calculated mol wt/cross- link (M_c)	549*	507*	525*
Calculated adiabatic temp rise from azide rearrange- ment ($^{\circ}\text{F}$)	498	240	345
Polymer melting temp ($^{\circ}\text{F}$)	--	~350	~350

*Variation occurs in the values for M_c because two isocyanates of different molecular weights and in different ratios are being jointly used in Cases 2 and 3.

It can be seen from Table I that Case 2 offers the best choice with respect to adiabatic temperature rise. This rise of 240°F would occur from the initiation temperature of about 175°F , giving a final temperature of 415°F . Such a final temperature should be tolerated by aluminized H Film but would be severe for aluminized Mylar. No relief can be obtained by going to a higher prepolymer of HP-370, both because the theoretical gel point is at $-\text{NCO}/-\text{OH} = 0.58$ and because we find experimentally that the Case 2 prepolymer is already somewhat too viscous for suitable frothing in a vacuum foaming process. The prepolymer of Case 3 has viscosity properties more suited to vacuum foaming, but at the expense of a 100 degree higher adiabatic temperature rise than Case 2.

Methods of solving the problems indicated above are being experimentally investigated. Some of these methods are as follows:

- (1) Reduction in cross-link density to whatever extent is permissible in view of the concomitant tendency to reduce the foam heat distortion temperature. This can be effected by one or more of the following:
 - (a) Use of a polyisocyanate of higher equivalent weight, e. g., MDI in place of TDI in a prepolymer or Structure XI in place of X in a precoat formulation.
 - (b) Use of a polyol resin of somewhat higher equivalent weight.
 - (c) Formulation of precoat to final $-\text{NCO}/-\text{OH}$ ratios less than 1.0, thus requiring less azide.
- (2) Use of lower viscosity polyols which would yield prepolymers of suitable viscosity at $-\text{NCO}/-\text{OH} = 0.4$ to 0.5 .

In the above discussion, it will be noted that an adiabatic process (and maximum temperature rise) is postulated for azide rearrangement. Some experimental vacuum foaming has been done in the past in which nearly isothermal operation

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at triggering temperature was the target. The following are some of the problems that are inherent in this approach:

- (1) The laboratory process should be set up to effectively simulate the rates of heat gain or loss that would prevail in orbit.
- (2) The process would necessarily be slow until perhaps half the azide had been rearranged because of the high temperature coefficient of azide rearrangement rate at 175°F and above. (Information on temperature coefficients was obtained early in the present reporting period; although it is incomplete and covers only the azides available at the time, it is believed to establish the situation.)
- (3) A slow foaming process allows time for drainage of cell walls under gravity and surface tension forces.
- (4) In slow foaming with radiant heating on the back side of the mirror-to-be, the first foam rising tends to form an insulating blanket that isolates unreacted or reacting precoat beneath. This changes the factors that control an isothermal operation.

It has seemed desirable to give major consideration to a fast foaming process that would be nearly adiabatic in vacuum.

D. VACUUM FOAMING OF PRECOATS CONTAINING STRUCTURE X AND A BLOCKED ISOCYANATE

1. General

In recent work, some study has been given to a precoat foam system containing two components that would each yield reactive diisocyanate when heated. One component is azide Structure X; the other is the bisphenol adduct of 4,4'-diphenyl methane diisocyanate. The formulation of the precoat then involves the following considerations:

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- (1) A prepolymer is chosen on the basis of (a) suitable viscosity at the critical stage in foaming and (b) structure to yield a final suitable M_c value for resistance to heat distortion.
- (2) The sum of azide and blocked isocyanate is chosen to supply the desired final $-NCO/-OH$ ratio. Isocyanate from azide is generally put around one third to one half of the total supplied.
- (3) The amount of azide is adjusted so that its rapid rearrangement will give an adiabatic temperature rise from 175 - 190°F into the range at which the blocked isocyanate is rapidly "unblocked" (with absorption of heat). At the same time the azide supplies blowing gas.
- (4) Catalysts for the urethane reaction are supplied so that good curing will occur in the short period of time at maximum temperature and thereafter.

2. Process Conditions

The time-temperature relation for the process is illustrated in Figure 1, which shows temperature observed by a thermocouple embedded in the precoat. Precoat was spread on the aluminized Mylar film to a loading of approximately 0.4g/in.² (see Figures 2 through 6). The precoated film was placed horizontally, precoat up, in a bell jar, evacuated to below one micron, and the process initiated by heating from above with the radiation from quartz-jacketed tungsten filament lamps. Evacuation and heating were done with a loose-fitting, perforated clear Mylar "back flap" (one mil thickness) in place. Spaced about an inch below the precoated film was a reflective surface to aid in approximately maintaining adiabatic conditions during the foaming.

The process may be broken down into the three time periods indicated in Figure 1. A short preheating period is required to come up to 175 - 190°F. Usually 7 to 10

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PRECOAT FORMULATION 382-21

BELL JAR FOAMING RUN NO. 1

TEMPERATURE RECORDED BY THERMOCOUPLE BURIED IN
PRECOAT MATERIAL ON ALUMINIZED MYLAR FILM

PRECOAT WT 0.3 G/IN.²

VACUUM { < 1 MICRON AT START
20 MICRONS MAX DURING FOAMING

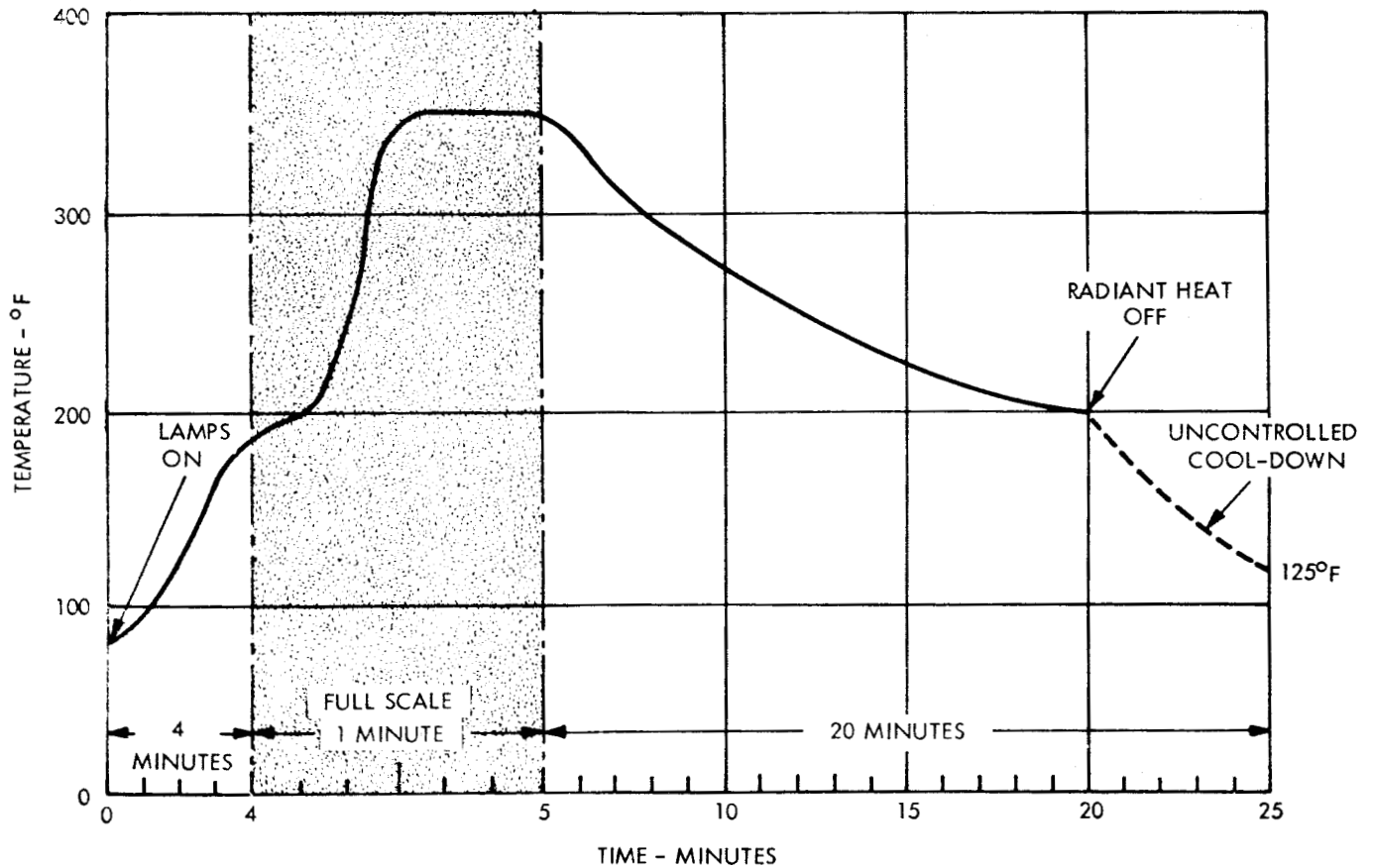


Figure 1. Temperature History of Precoat Foam Reaction

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Figure 2. Preparation of 6-Inch Disc Test Sample - Precoat Foam on Aluminized Mylar

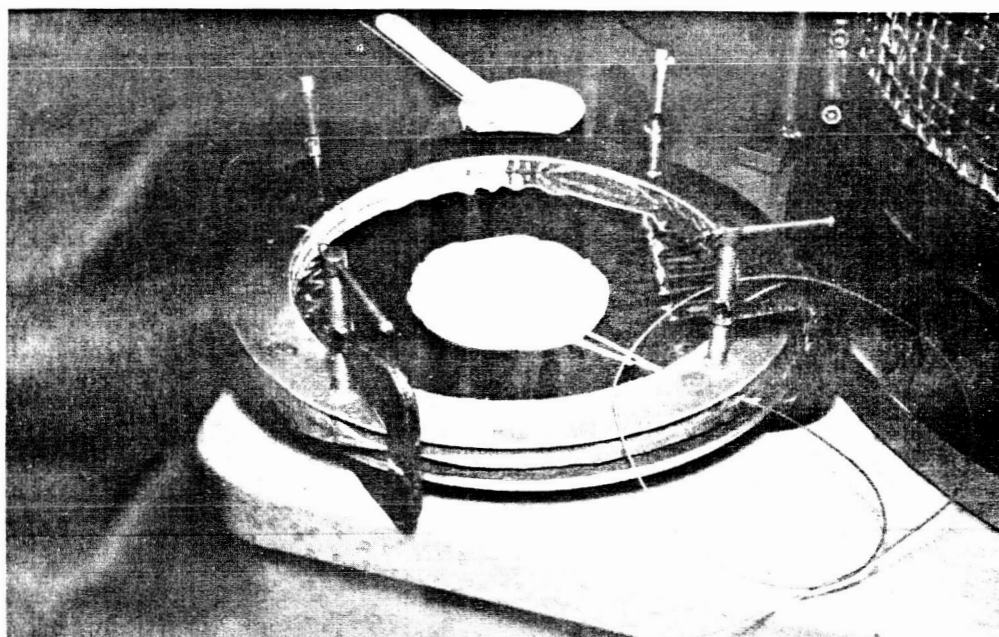


Figure 3. Test Sample in Ring Fixture

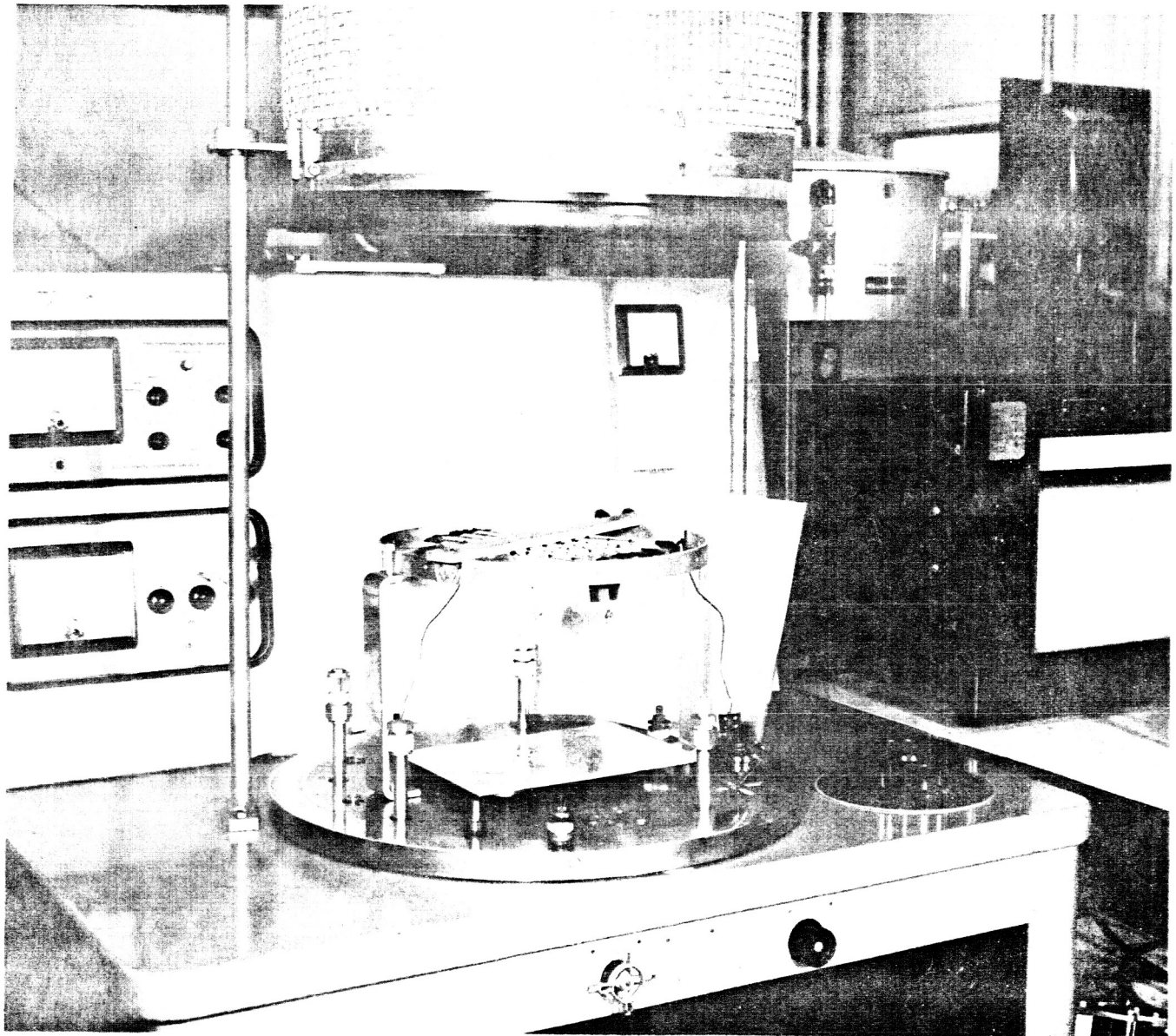


Figure 4. Bell Jar Test Facility

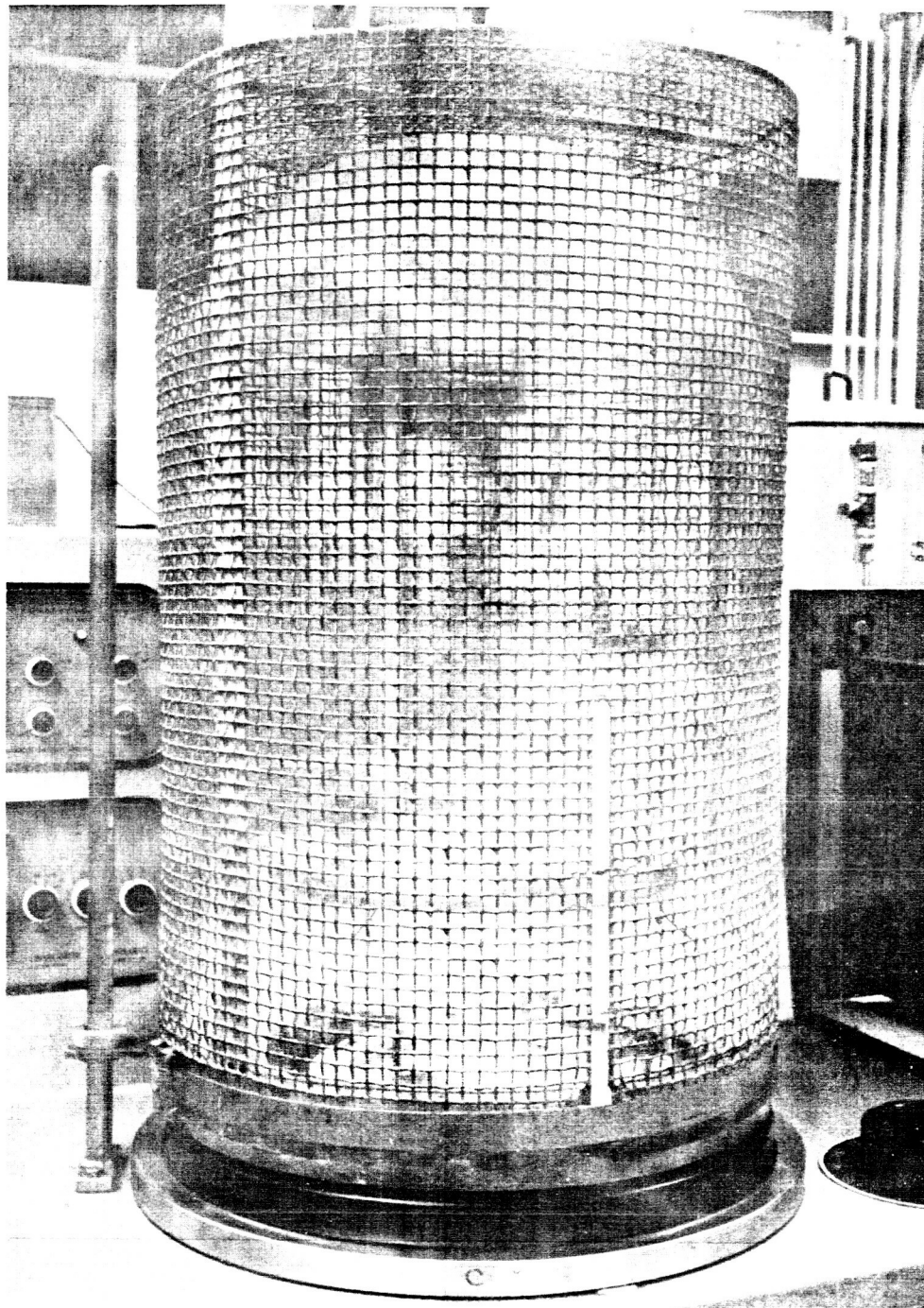


Figure 5. Test Run in Evacuated Bell Jar
with Heat Applied

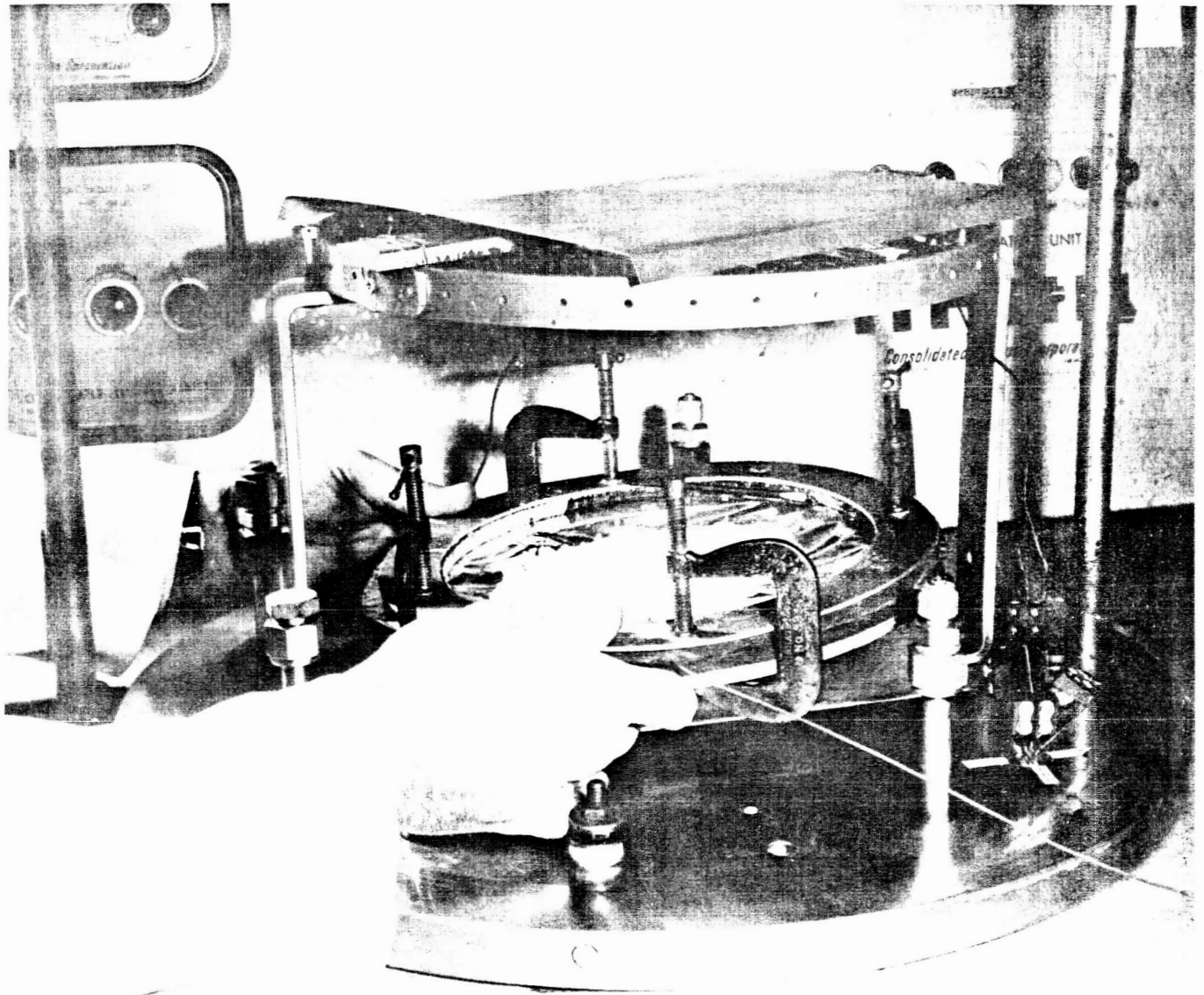


Figure 6. Removal of Test Sample from Bell Jar

minutes are allowed for this, although it was done in 4 minutes in the subject run. The preheating suffices to initiate a rapid, self-propagating rearrangement of the azide with heat release sufficient to carry the foaming mass to about 350°F. The third period is the subsequent slow cooling with reduced radiation from the lamps. Late in the second period and early in the third period, some condensation occurs on the cool inner surface of the wall of the bell jar, which is taken to be phenol. This is presumed to vaporize after the blocked isocyanate has been thermally decomposed, freeing phenol. During the second period, after the release of the major part of the blowing gas, polymer cure is advanced to the point that no further rise of froth occurs and rigidization proceeds rapidly. Further curing is believed to occur in the first few minutes of the third period.

3. Blocked Isocyanate Properties

The choice of the bisphenol adduct of 4,4'-diphenyl methane diisocyanate for use is largely based on the following considerations:

- (1) The diisocyanate when freed has high reactivity and rather low volatility, and because of its structure, enhances the heat distortion resistance of a polyurethane containing it.
- (2) The stability of the blocked structure appears to be sufficient that a precoat containing it should be stable in storage for extended periods of time. The thermal stability under short-term heating is illustrated by the differential thermal analysis curve shown in Figure 7. This curve was obtained at a heating rate of 10°C/min on a sample of the pure material (DuPont's commercial product, designated Hylene MP). It is seen that no reaction occurs in the DTA until above 200°C, where the first endothermic peak (between 207 and 217°C) is taken to signal the breaking up of the adduct. This considerable degree of thermal stability is advantageous, since it has been noted that blocked isocyanates

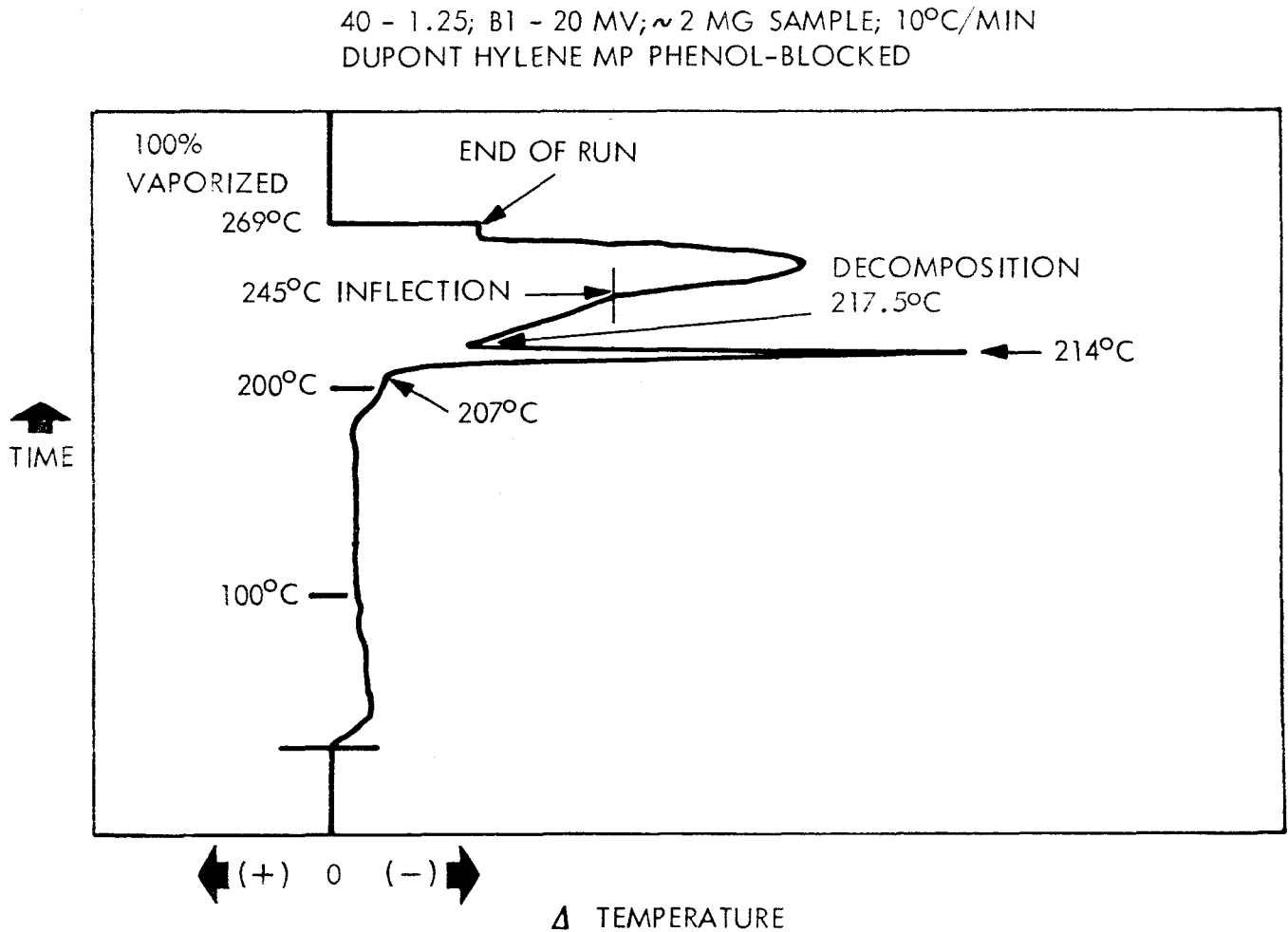


Figure 7. Differential Thermal Analysis Curve of Hylene MP

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tend to have less stability in the presence of polyol resins. This is borne out by the differential thermal analysis curve shown in Figure 8, which was run on a mixture containing 27 weight percent of the blocked isocyanate together with a hydroxyl-terminated prepolymer and the catalysts and surfactants that would be employed in a precoat formulation. Superimposed on the very large endothermic area beginning almost at the start of the run, there is a smaller endothermic peak initiated at about 128°C and peaking at 147°C that is taken to indicate the "unblocking" reaction. This interpretation is supported by observations made of low degrees of cure in precoat formulations containing azide and phenol adduct that were slowly heated with absorption of exothermic heat, so that the temperature never exceeded 210°F (see Figures 9 and 10). In these cases it is believed the phenol adduct did not appreciably decompose. (Some further DTA work is contemplated.)

- (3) The commercial availability of this blocked isocyanate and the favorable report by DuPont on its stability in the presence of water.

4. Storage Stability Tests

Two precoat formulations employing Structure X and the blocked isocyanate (Hylene MP) have been made up and put into dark storage at room temperature. These will be held at least one month before the first inspection. Quantities are sufficient that it will be possible to carry the tests over at least three months.

5. Precoat Formulations and Vacuum Foaming Results

A group of formulations and results obtained in vacuum foaming (vacuum from <1 to ~50 microns at momentary peak) are reported in Table II. The formulations generally contained the proper amount of Structure X so that the exotherm on rapid foaming would peak at about 350°F. Final -NCO/-OH ratios are in the range of 0.85 to 1.0.

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- A. APPARENT DECOMPOSITION OF HYLENE MP AT 126°C AND IS MOST RAPID AT 147°C.
- B. MAJOR TRANSITION BEGINS AT 195°C IN THE EXOTHERMIC DIRECTION INDICATED BY UPWARD SHIFT OF BASE LINE.

PEP 650 POLYMER 55 (PBW)
L5310 3
DABCO 3
TIN(D-22) 1
HYLENE MP 27

NITROGEN ATMOSPHERE - 2" HG
40 - 1.75
10°C/MIN
SIGNAL AMPL - 40μV
SAMPLE SIZE - 30 MG

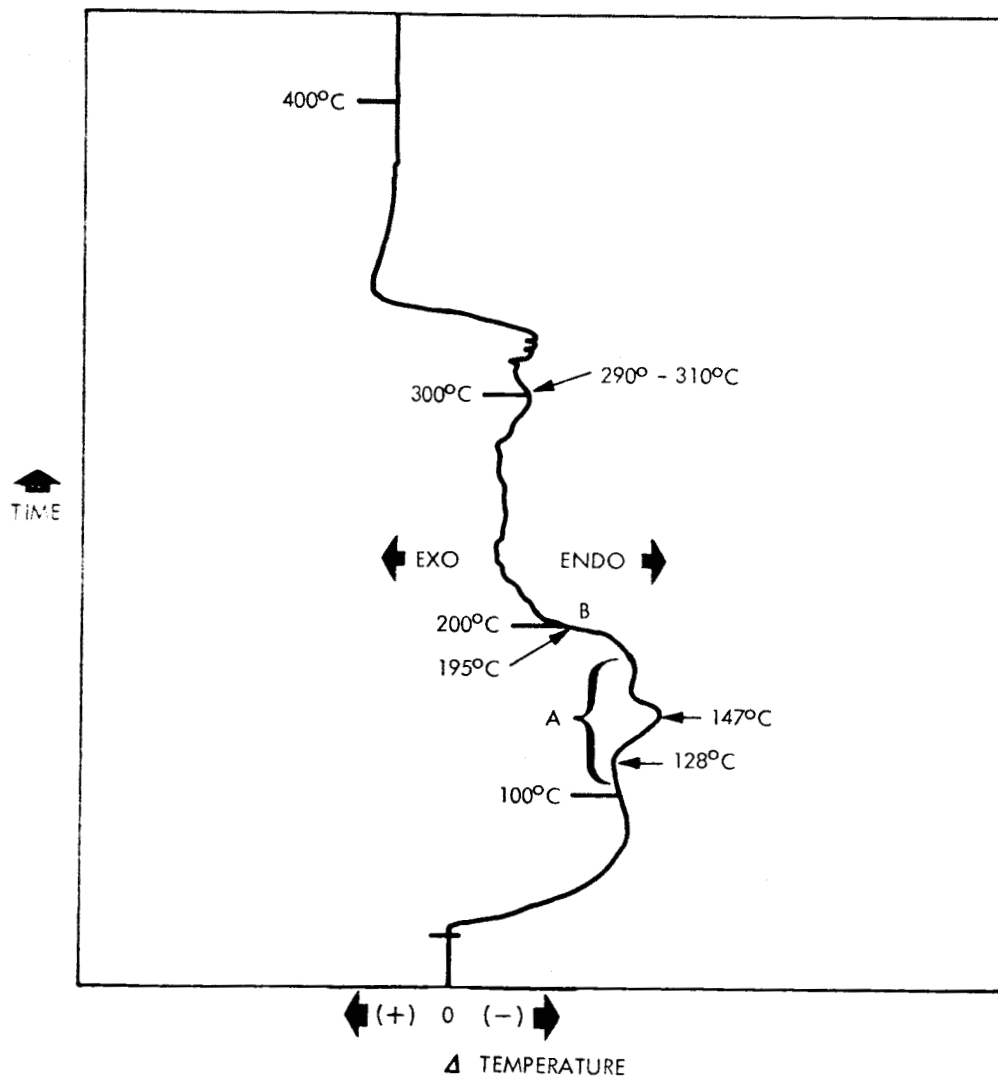


Figure 8. Differential Thermal Analysis Curve of Prepolymer Mixture

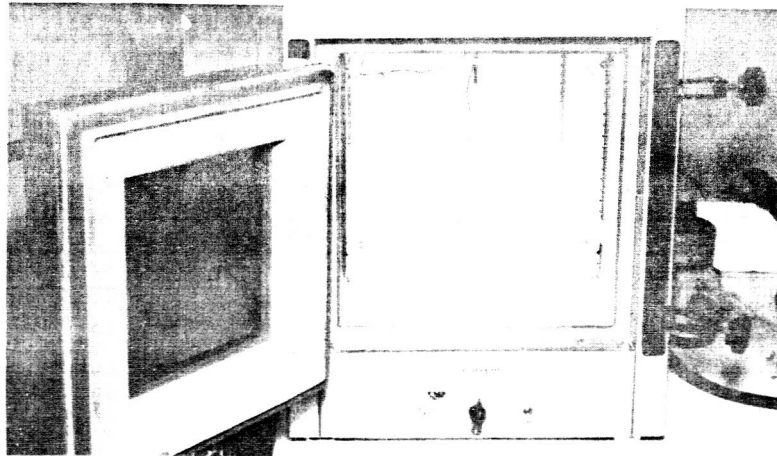


Figure 9. Vacuum Oven showing Test Sample with Thermocouple

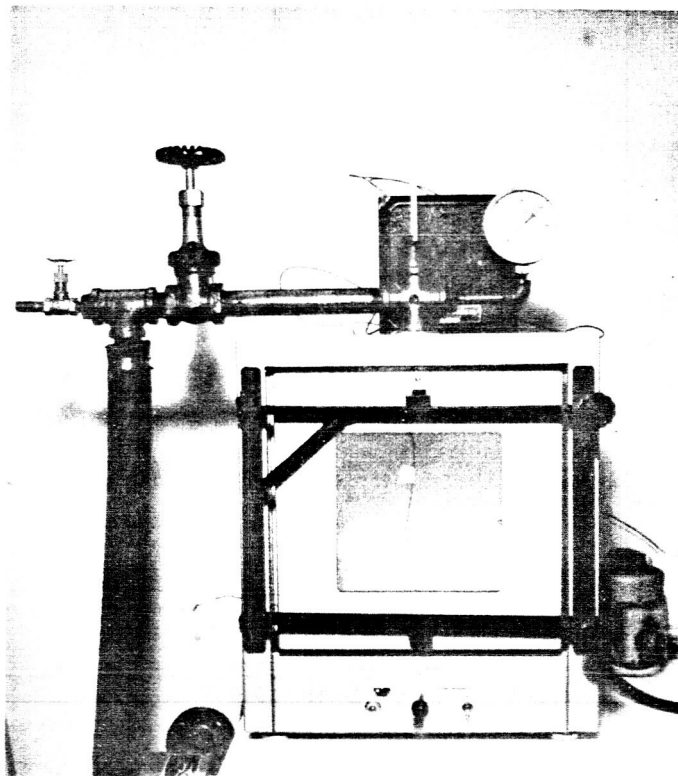


Figure 10. Vacuum Oven for Experimental Tests in Foam Formulation

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Table II. Precoat Formulations and Vacuum Foaming Results

Formulation No.	382-9 No. 5	382-14	382-15	382-16 No. 1	382-16 No. 2	382-21	382-23
Type or Basis of prepolymer	TP 440(c) + TDI	HP-370(f) + IDI	HP-370(f) + TDI	PEP 650(g) + TDI	PEP 650(g) + TDI	PEP 650(g) + TDI	Polymer mix of HP-370 + PEP 650 after prepolymerization
Prepolymer -NCO/-OH	0.33	0.33	0.33	0.33	0.33	0.4	0.33
Wt % of prepolymer	48	56.25	51.4	50.5	50.8	57	50.8
Azide Structure	X	I	X	X	X	X	X
Wt % azide	16.7	11.3	15.4	15.9	15.8	16.2	15.8
Wt % blocked isocyanate(a)	23.8	29.6	26.6	27.1	26.8	19.4	26.8
Wt % Surfactant(b)	0.5	0.56	1.54	1.5	1.5	1.7	1.5
Catalyst							
Wt % Dabco(c)	1.5	0.56	1.54	1.5	1.5	1.7	1.5
Wt % D-22 tin(d)	0.5	0.56	0.51	0.5	0.5	0.57	0.5
Wt % Dipropylene glycol	3.0	1.14	3.8	3.0	3.0	3.46	3.0
Maximum measured temp (°F)							
During foaming		Little rise in temp	340	346	325	350	345
Condition of mirror surface		Good	Good	Good to fair	Good to fair	Good	Good to excellent
Foam properties							
Polymer melt temp (°F)		240 - 250	260 - 290	250 - 265	250	215 - 230	270 - 285
Frothing prior to cure	Very fluid mix. Much expansion and collapse.	Rather stiff. Poor foam due to heat on foam before cure.	Slightly more fluid, but a little too stiff.	Rather fluid, but borderline.	Rather fluid, but still borderline.	Still slightly fluid.	Close to ideal. Very slightly stiff.

(a) Blocked diisocyanate used in all cases was the bisphenol adduct of 4,4'-diphenyl methane diisocyanate, under the commercial designation of Hylene MP by DuPont.

(b) Surfactant used in all cases was L-5310, Union Carbide Corp.

(c) The amount of Dabco used in all cases was added as a 33% solution in dipropylene glycol, made by Houdry Process Corp.

(d) D-22 tin catalyst is dibutyl tin dilaurate in an inert solvent, made by Union Carbide Corp.

(e) A polyether triol supplied by Wyandotte Chemical Corp.

(f) A polyether tetrol supplied by Corn Products Co.

(g) A polyether tetrol supplied by Wyandotte Chemical Corp.

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From these tests and other work, the following comments may be made:

- (1) Foam structure appears to be very much influenced by viscosity of the frothing mass during the second period of the process and less certainly by use of a surfactant. As is to be expected from the large nitrogen gas release from azide, a very open-cell structure is the rule. In all cases, some "orange peel" appears on the mirror surfaces.
- (2) The time required for the process is less than the light period of a single earth orbit.
- (3) Since 300°F should be sufficient to decompose the blocked isocyanate, the maximum temperature of the process might be reduced to 300°F, with some lengthening of the time at or near 300°F to ensure sufficient time for decomposition and ensuing reaction of the freed diisocyanate. Foams made under schedules such as in Figure 1 have in some cases had their polymer melt temperature raised about 25°F by a 72-hour post-cure at approximately 215°F in atmosphere. In other cases, such a post-cure caused no change in polymer melt temperature.
- (4) Preliminary results of analyses of the vacuum foams for organic nitrogen give little indication that the nitrogen-containing reactant (isocyanate) is being lost to the vacuum. Low loss to vacuum has already been established for the prepolymers, so that the retention of reactants during foaming now appears to be achieved. Weight losses from vaporization of phenol, possible vaporization of catalyst solvent and surfactant, and from release of azide nitrogen do occur.

E. ADVANCED MATERIALS - FILM SUBSTRATE AND ADHESIVE

The range of temperatures arrived at by the production of the polyurethane rigidizing foam has suggested the use of a film material having more desirable high

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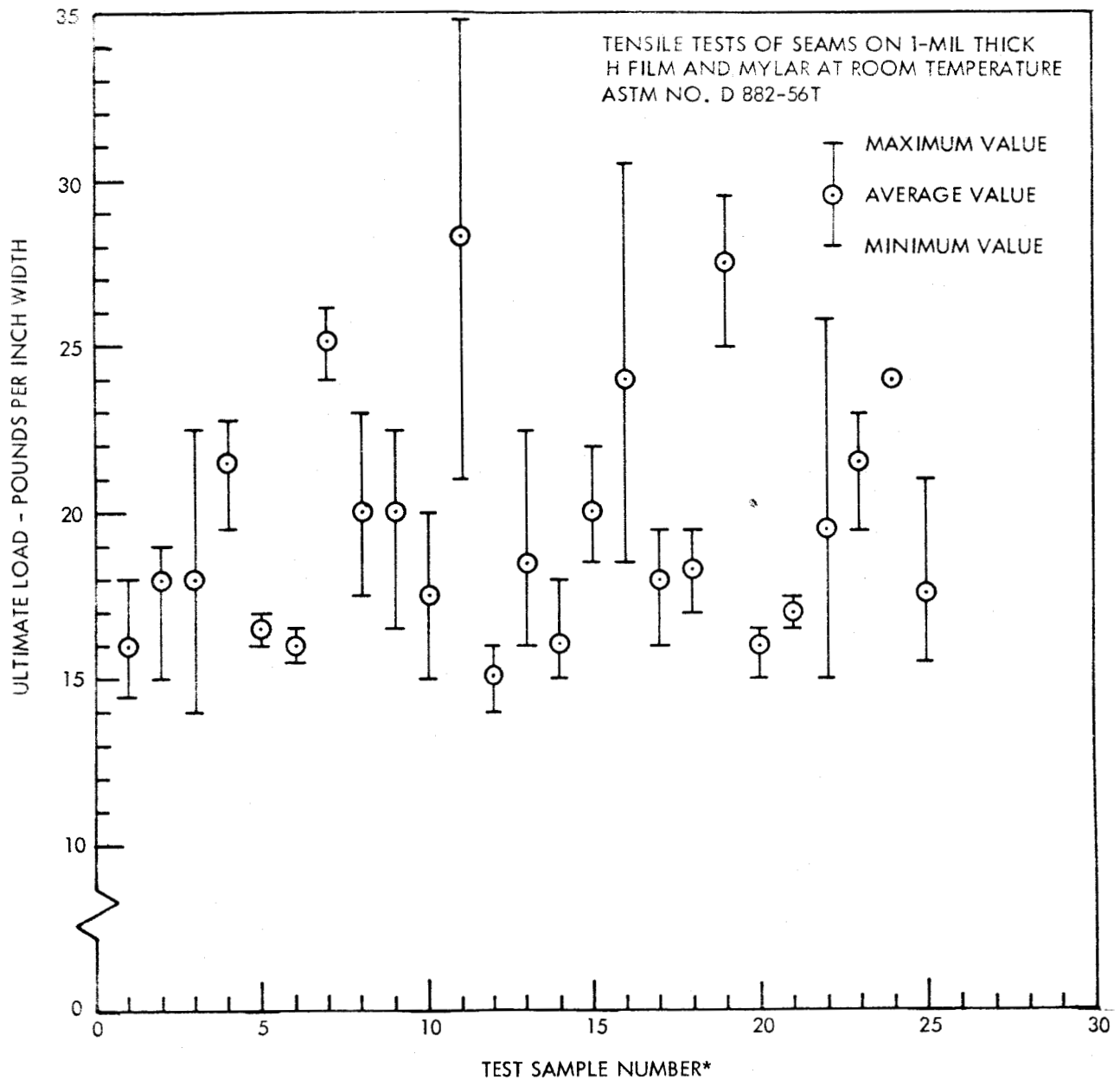
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temperature properties than Mylar. The film most suitable for this requirement may be DuPont H Film (sometimes called H Mylar or high temperature Mylar). It has room temperature properties similar to that of Mylar, but it also has a high degree of thermal stability. The physical properties are given in Appendix B.

To fabricate representative size mirrors with H Film, it was necessary to investigate the effectiveness of various adhesives and their adaptability to the production of paraboloidal mirrors which would be rigidized in space with a predistributed foam material.

A number of adhesive materials were selected for test. Seams were made on one-inch wide strips of H Film. After curing, the strips were subjected to tensile testing at room temperature (see Figure 11 for results). The test strips were then exposed to a temperature environment of 400°F and tensile tested (see Figure 12 for results). A selected number of these adhesives will be later subjected to a temperature environment of 500°F and tensile tested.

The data obtained to date gives favorable indication that a suitable material and adhesive may be available as a film substrate for the predistributed foam rigidizing process.

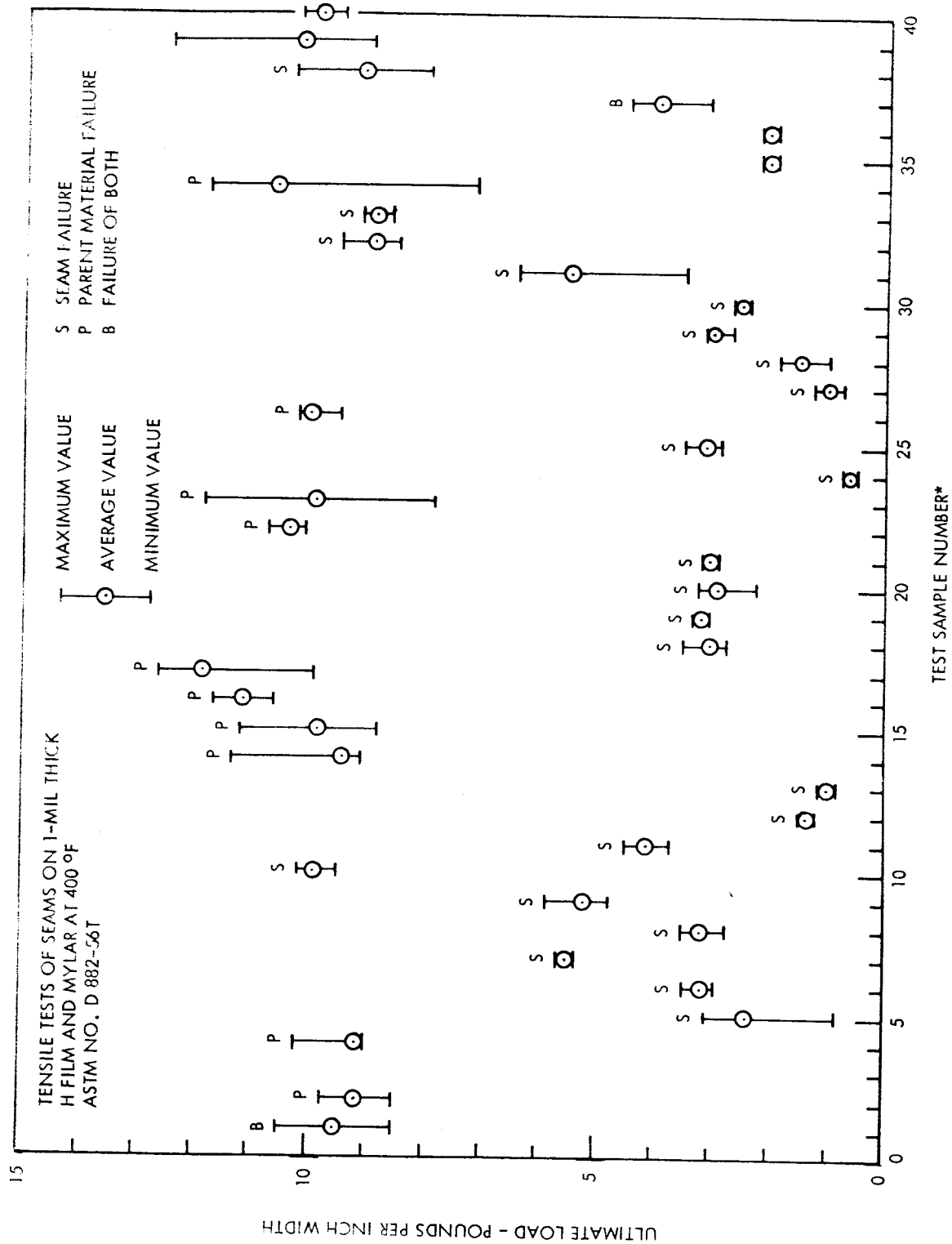


*SEE TABLE III FOR DESCRIPTION OF TEST SAMPLES.

Figure 11. Film Seam Shear at Room Temperature

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*SEE TABLE III FOR DESCRIPTION OF TEST SAMPLES.

Figure 12. Film Seam Shear at 400°F

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Table III. Test Sample Description

Sample No.	Description
1	H Film seamed with 5% DuPont polyester adhesive No. 46971; single surface, one coat; ironed at 325°F.
2	H Film seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, one coat; ironed at 325°F.
3	H Film seamed with 5% DuPont polyester adhesive No. 46971; single surface, two coats; ironed at 325°F.
4	H Film seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, two coats; ironed at 325°F.
5	Mylar seamed with 5% DuPont polyester adhesive No. 46971; single surface, one coat; ironed at 325°F.
6	Mylar seamed with 5% DuPont polyester adhesive No. 46971; single surface, two coats; ironed at 325°F.
7	Mylar seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, two coats; ironed at 325°F.
8	H Film seamed with 301 Schjelbond adhesive; ironed at 325°F.
9	Mylar seamed with 301 Schjelbond adhesive; ironed at 325°F.
10	H Film seamed with 101 Schjelbond adhesive; ironed at 325°F.
11	Mylar seamed with 101 Schjelbond adhesive; ironed at 325°F.
12	H Film seamed with Bloomingdale Rubber adhesive No. BR-1000; single surface, one coat; ironed at 325°F.
13	H Film seamed with Bloomingdale Rubber adhesive No. BR-1000; both surfaces; one coat; ironed at 325°F.
14	H Film seamed with 5% DuPont polyester adhesive No. 46971; single surface, one coat; vacuum applied at 325°F.
15	H Film seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, one coat; vacuum applied at 325°F.
16	H Film seamed with 5% DuPont polyester adhesive No. 46971; single surface; two coats; vacuum applied at 325°F.

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Table III. Test Sample Description (Continued)

Sample No.	Description
17	H Film seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, two coats; vacuum applied at 325°F.
18	Mylar seamed with 5% DuPont polyester adhesive No. 46971; single surface, two coats; vacuum applied at 325°F.
19	Mylar seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, two coats; vacuum applied at 325°F.
20	H Film seamed with 301 Schjelbond adhesive; vacuum applied at 325°F.
21	Mylar seamed with 301 Schjelbond adhesive; vacuum applied at 325°F.
22	H Film seamed with 301 Schjelbond adhesive; vacuum applied at 325°F.
23	H Film seamed with Dow Corning 131 Silastic adhesive; both surfaces, one coat; vacuum applied at 325°F.
24	H Film seamed with Bloomingdale Rubber adhesive No. BR-1000; single surface, one coat; vacuum applied at 325°F.
25	H Film seamed with Bloomingdale Rubber adhesive No. BR-1000; both surfaces, one coat; vacuum applied at 325°F.
26	H Film seamed with Dow Corning 131 Silastic adhesive; both surfaces, one coat; ironed at 325°F.
27	H Film seamed with Bloomingdale Rubber adhesive No. BR-1000; single surface, two coats; ironed at 325°F.
28	H Film seamed with Bloomingdale Rubber adhesive No. BR-1000; both surfaces, two coats; ironed at 325°F.
29	Mylar seamed with 5% DuPont polyester adhesive No. 46971; single surface, one coat; vacuum applied at 325°F.
30	Mylar seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, one coat; vacuum applied at 325°F.
31	Mylar seamed with 101 Schjelbond adhesive; vacuum applied at 325°F.
32	H Film seamed with Don Corning 131 Silastic adhesive; single surface, one coat; vacuum applied at 325°F.

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Table III. Test Sample Description (Continued)

Sample No.	Description
33	H Film seamed with Dow Corning 131 Silastic adhesive; single surface, two coats; vacuum applied at 325°F.
34	H Film seamed with Dow Corning 131 Silastic adhesive; both surfaces, two coats; vacuum applied at 325°F.
35	H Film seamed with Bloomington Rubber adhesive No. BR-1000; single surface, two coats; vacuum applied at 325°F.
36	H Film seamed with Bloomington Rubber adhesive No. BR-1000; both surfaces, two coats; vacuum applied at 325°F.
37	Mylar seamed with 5% DuPont polyester adhesive No. 46971; both surfaces, one coat; ironed at 325°F.
38	H Film seamed with Dow Corning 131 Silastic adhesive; single surface, one coat; ironed at 325°F.
39	H Film; no seam; longitudinal.
40	H Film; no seam; transverse.

SECTION III - SUMMARY OF WORK FOR THE NEXT QUARTER

Production of samples from various polyol resins, prepolymers, and diisocyanates (primarily MDI) will be given physical tests for heat distortion temperature and strength. It is desired to establish the range of compositions and final -NCO /-OH giving acceptable heat distortion and strength properties.

Continued study of composition and process factors with the objective of refining cell structure and controlling density in vacuum foaming.

Accumulation of information on stability in storage of blocked isocyanate compounded in precoat formulations.

Extension of vacuum foaming studies to production of 2-foot diameter foamed mirrors.

Begin Phase II - physical testing.

APPENDIX A. PROPERTIES OF AZIDE AND RESIN MATERIALS

1. AZIDE MATERIALS

Table A-1 is a summary of molecular structures, physical properties, and other information for Structures I, X, XI, and XII (the last is yet to be successfully synthesized).

A summary of information on the rate of azide rearrangement at constant temperature for Structures I, X, and XI is given in Table A-2. Results with Structure X seem acceptable in view of the probable experimental errors in initial work with the azotometer. However, the results with Structures I and XI suggest that these materials may be of low purity (less than 90 percent pure) or that they do not undergo a near quantitative rearrangement reaction to the desired isocyanates. Further study is desirable, since either source of discrepancy would throw uncertainty into the equivalent weight to be used in precoat formulation.

Measurements of weight losses sustained over multihour exposures to high vacuum at 75 and 150°F of azides and polyol resins are given in Table A-3. The troublesome volatility of Structure I is evident, but Structures X and XI appear much better.

2. RESIN MATERIALS

Table A-4 reports properties of the two polyether polyol resins newly used in the program. It is to be noted that their viscosities at room temperature are only a few percent of the values for previously used polyol resins; at the same time, density of hydroxyl groups available for reaction with isocyanate is in the same range as for the more viscous polyols.

The hydroxyl terminated prepolymers whose preparation, stoichiometry, and properties are outlined in Table A-5 are made by reacting a specified polyol resin with some fraction of the equivalent amount of a polyisocyanate as such (not as derived in situ from an azide) (see Figure A-1). The product is then of higher molecular weight than the original polyol resin, but is still a polyol in the sense that its reactive groups are hydroxyls that were in excess of the isocyanate used. (This is the opposite situation from commercial, mechanically-mixed foams, where partial polymers with isocyanate terminations are known as prepolymers.)

The present objective is to incorporate as great a fraction of the isocyanate equivalent of the resin into the prepolymer as is feasible. The maximum that can be incorporated is of course determined by the rate at which build-up in molecular weight and chain branching changes prepolymer properties from a viscous liquid to a high melting, intractable solid. Theory also indicates limits, varying with functionality of each reactant, at which the gel point will be encountered and the prepolymer will become intractable.

APPENDIX A

Table A-1. Properties

Structure	Azide Name and Mol Structure	Azide Functionality	Isocyanate Produced on Rearrangement
I	<p>Terephthaloyl Azide</p> $\text{N}_3\text{OC}-\text{C}_6\text{H}_4-\text{CON}_3$ <p>Mol wt = 216</p>	2	1, 4 - Benzene Diisocyanate
X	<p>4, 4' -Diphenyl Methane Diacyl Azide</p> $\text{N}_3\text{OC}-\text{C}_6\text{H}_4-\text{C}(\text{H})_2-\text{C}_6\text{H}_4-\text{CON}_3$ <p>Mol wt = 306</p>	2	<p>4, 4' -Diphenyl Methane Diisocyanate</p> <p>Mol wt = 250 Amine eq = 125</p>
XI	$\text{N}_3\text{OC}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}(\text{CH}_2)_6-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{CON}_3$ <p>Mol wt = 464</p>	2	<p>--</p> <p>Mol wt = 408 Amine eq = 204</p>
XII	$\begin{array}{c} \text{H}_2\text{C}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}_2 \\ \\ \text{N}_3\text{OC}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH} \\ \\ \text{N}_3\text{OC}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}_2 \end{array}$ <p>Mol wt = 1006</p>	4	<p>--</p> <p>Mol wt = 894 Amine eq = 224</p>

**Assuming a unimolecular reaction, the time for 50 percent of the material to
† Experimental value adjusted for suspected low purity.

Properties of Acid Azides

Azide N Content (Wt %)		Azide Melting Point (°F)	Crystal Density of Azide (g/cc)	Half Life** at Stated Temperature (min)	Heat Release on Rearrangement at 275°F (cal/g)	Remarks Pertaining to Azides
Total	Releasable					
38.9	25.9	230-232	1.58	28 (prelim) at 196°F †	282	Can be detonated by rapid heating.
27.4	18.3	181-184 (dec)	1.34	30 (prelim) at 193°F	224	Have not observed detonation on rapid heating.
18.1	12.1	190-199 (dec)	1.31	24 (prelim) at 196°F †	115	Have not observed detonation on rapid heating.
16.7	11.1	--	--	--	--	No authentic material yet available.

undergo rearrangement as measured by nitrogen release.

Table A-2. Azide Decomposition Rates^(a) - Azotometer Measurements

Structure	I		X		XI	
Temperature (°F)	196	207	193	208	196	208
Time (minutes) for following percent decompo- sitions(b):						
25%	---	---	12	5	---	---
50%	28	13	30	11.5	24	10
75%	---	---	66	23	---	---

NOTE: The data in this table are preliminary, but serve the immediate purpose of establishing the rate of azide rearrangement versus temperature relationship.

(a) For data analysis, the following purities are tentatively assumed from internal and related evidence(c):

Structure I - 83%

Structure X - 100%

Structure XI - 85%

(b) Times are read from plotted curves of gas production versus run time; a correction is applied for hold-up in the system, leading to an apparent induction period.

(c) Since making the above azotometer measurements, brief attention has been given the question of whether azide purity can be easily assayed by rearranging the material, dissolved in a solvent, and then employing the n-dibutylamine titration method to determine the amount of isocyanate produced from a known weight of azide material. However, it was found that at least three variables were present simultaneously: (1) azide purity, (2) a question of whether small amounts of azide were lost to non-isocyanate-producing side reactions, and (3) rather frequent occasions in which products of the rearrangement were not completely soluble in the solvent system of the analytical method. It was established that 86 to 93 percent of the theoretical yield of isocyanate could be obtained from Structure I and 90 percent from Structure X. Structure XI gave only slightly soluble products and 5 - 10 percent of theoretical yield of isocyanate, which reflects incompatibility with the assay method.

Table A-3. Subliming Rates of Azides and Resins in High Vacuum

Percent Weight Loss ^(a) (Accumulated)				
Hours at 75°F	Structure I	Structure X	Structure XI	MDI ^(b)
17	37	--	--	--
17.5	--	0.3	0.3	--
23	--	--	--	8.1
40.5	--	1.6	0.8	--
84.5	77	--	--	--
132.5	82	--	--	--

Hours at 75°F	PFR-6 Resin	RS-375 Resin	Precoat ^(c)
1.1	--	--	4.5
17	1.1	0.1	--
23	--	--	6.4
84.5	3.2	0.7	--
90.5	--	--	7.6
132.5	3.4	0.5	--
Plus 72.5 hours at 150°F	13.4	3.9	--

(a) Weight losses on three individual samples, exposed simultaneously, are averaged.

(b) This material, 4, 4'-diphenyl methane diisocyanate, is of interest as it is the diisocyanate resulting from the rearrangement of Structure X.

(c) Formulation containing small amount of plasticizing acetone (most volatile component), 20 wt in percent Structure I as wetted solids, and the balance viscous low prepolymer of PFR-6 and tolylene diisocyanate.

Table A-4. Typical Physical Properties of Polyether Polyol Resins

Properties	TP 440	PEP 650
Average Molecular Wt	418	600
Hydroxyl No. KOH/g	404	374
Water, % max	0.1	0.1
Unsaturation, meq/g	0.005	0.004
Volatiles, % by weight	0.2	0.01
Sodium and Potassium, ppm	70	50
Acid Number	0.03	0.03
Visc at 25°C, cps	625	1140

1. Physical properties and material supplied by Wyandotte Chemical Corp, Wyandotte Michigan.
2. TP 440 is trimethylol propane based, propylene oxide extended, polyether triol.
3. PEP 650 is a pentaerythritol based, propylene oxide extended, polyether tetrol.

Table A-5. Preparation of Prepolymers

Polymer Run No.	59B(a)	60(b)	61(b)	62	63	382-4	382-7	382-10	382-11	382-21	382-25
Resin Used	PFR-6	PFR-6	PFR-6	PFR-6	HP-370	PFR-6	TP-440	PEP 650	HP-370	PEP 650	PEP 650
Diisocyanate Used	TDI	TDI	TDI	MDI	TDI	TDI	TDI	TDI	TDI	TDI	MDI
NCO/OH (Mole Ratio Used)	0.62	0.70	0.75	0.70	0.55	0.24	0.33	0.33	0.33	0.4	0.3-0.4
NCO/OH (Theo. Mole Ratio For Gel Point)	0.72	0.72	0.72	0.72	0.58	0.72	0.72	0.58	0.58	0.58	0.58
Type of Polymerization	Reactants dissolved in approximately 3 times their weight of acetone, mixed, and held in closed container several days at room temperature; 0.1% tin catalyst (D-22) added and never neutralized.					Temperature of 120°C for 2 hrs under dry nitrogen atmosphere with stirring					
Resultant Prepolymer	Firm gel occluding all acetone <					Let down with acetone after polymerization					
PMT (Dried Acetone Free) or Eqv Wt of Prepolymer	200 to 215°F	---	210 to 230°F	---	~150°F	180(c)	256.5(c)	268(c)	268(c)	372(c)	534 to 624(c)
(a) Run 59 was made with the same reactants and reactants' ratio as shown above for 59B, but no solvent was used. The product was an intractable, horny solid, PMT around 225°F, apparently partially cross-linked. (b) The swollen, rubbery gels from Runs 60 and 61 were not acetone soluble and could be broken down mechanically only with difficulty. (c) Equivalent wt of prepolymer. Grams of prepolymer needed to react with 1 eqv of isocyanate containing material, e.g., 108 grams Structure I, 153 grams Structure X, etc.											

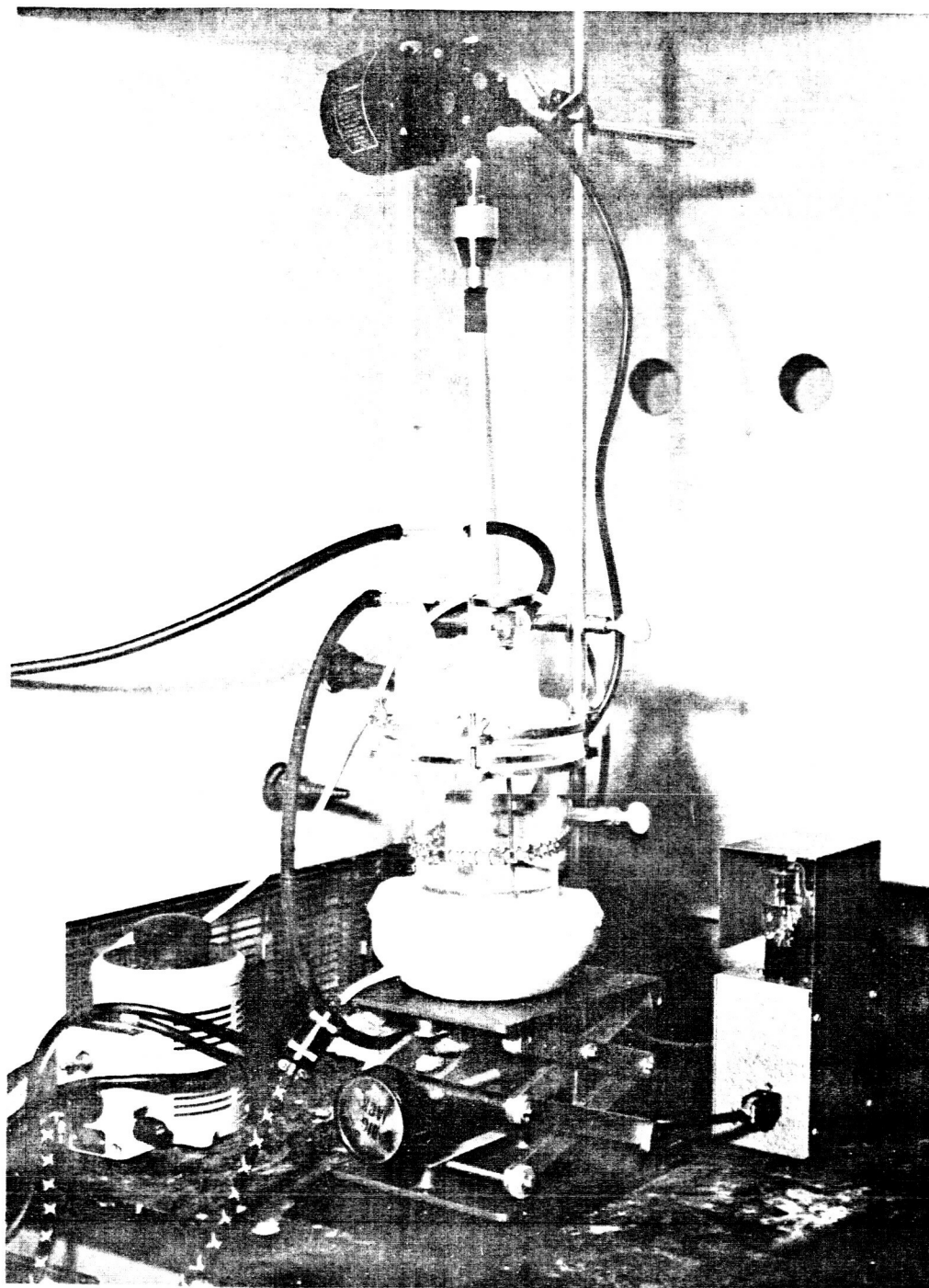


Figure A-1. Resin Kettle Used for Preparing Prepolymers

APPENDIX B. PHYSICAL PROPERTIES OF H FILM*

H Film is the designation for a new high-temperature polyimide film under development by DuPont. H Film is currently available in experimental quantities. Market development quantities should be available in the latter half of 1964.

H Film possesses a unique combination of properties hitherto unavailable in an organic polymer film (see Table B-1). This infusible, intractable polymeric film, which is relatively stiff and extremely tough, has room temperature properties similar to those of Mylar. It exhibits an extremely high degree of thermal stability and also maintains flexibility at cryogenic temperature.

A significant advantage of H Film over currently available materials is the retention of properties over a wide temperature range. For example, at 4°K, H Film can be bent around a 1/4-inch diameter mandrel without breaking, while at 500°C (932°F), it still exhibits a higher tensile strength (4500 psi) than polyethylene at room temperature (2500 psi). The modulus and tensile strength decrease almost linearly as the temperature is raised, while the elongation goes through a maximum value at 300°C (572°F). There is no indication of a second order transition up to 500°C, and this has been confirmed by dynamic mechanical methods.

Perhaps the most outstanding property of H Film is its stability at very high temperatures. For example, H Film has no melting point, is nonflammable, and only chars when exposed to a direct flame. Its zero strength temperature (the

*Information in this appendix was taken from "H Film - DuPont's New Polyimide Film" by W.E. Tatum, L.E. Amborski, C.W. Gerow, J.F. Heacock, and R.S. Mallouk, AIEE T-153-3, presented at Electrical Insulation Conference 17 September 1963 at Chicago, Illinois.

Table B-1. Typical Properties of H Film*

PROPERTY	ASTM NO.	UNITS	TEMP (°C)	VALUE**
Tensile Strength	D-638	psi	23	24,000
			200	17,000
Modulus	D-638	psi	23	415,000
			200	260,000
Elongation	D-638	%	23	65
			200	90
Stress at 3% Elongation	D-638	psi	23	14,000
Pneumatic Impact	DuPont	kg-cm/mil	23	6
Mullen Burst	D-774-46	psi	23	75
Dielectric Constant	D-150-59	--	23	3.5 (10 ³ cps)
Dissipation Factor	D-150-59	--	23	0.002 (10 ³ cps)
Volume Resistivity	D-257-61	ohm-cm	23	10 ¹⁸
Surface Resistivity	--	ohms	23	>10 ¹⁶
Dielectric Strength	D-149-59	volts/mil	23	7,000 (1/4" electrode)
Zero Strength Temp	DuPont	°C	--	815
Cut-Through Temp	DuPont	°C	--	>435
Coef of Thermal Conductivity		BTU-inch hr ft ² °F	23	1.0
Shrinkage	--	%	300	0.5
Thermal Coef of Expansion	D-696-44	cm/cm/°C	--	2.04 x 10 ⁵
Density	D-1505-57T	g/cc	2	1.42
Area Factor	--	ft ² /lb/mil	--	135
Moisture Absorption	--	%	23	1.3 (50% RH)
			23	3.0 (100% RH)
Coef of Hygroscopic Expansion	--	cm/cm/% RH	23	2.2 x 10 ⁵

*The values listed in this table are not specifications, but represent average values of experimental 1-mil film.

**Represents average of MD and TD values where applicable.

temperature at which a film strip fails in five seconds under a 20-psi load) is greater than 800°C (1472°F), some 250°C above that of aluminum. The cut-through temperature of H Film is above 435°C (815°F) and is measured by placing a weighted probe on the film at various temperatures until penetration of the film occurs. This last test demonstrates H Film's high resistance to deformation under load at elevated temperatures.

With respect to prolonged exposure at elevated temperatures, H Film is superior to any organic polymer film available. After eight weeks' exposure at 300°C (572°F), the volume resistivity is unchanged and the dielectric strength is 80 percent of the original value. Thermal aging of H Film to embrittlement (1 percent elongation) will require 10 years at 250°C (482°F), one year at 275°C (527°F), one month at 300°C (572°F), and one day at 400°C (752°F).

H Film absorbs about 1.3 percent water at 50 percent relative humidity and a maximum of 3 percent water at 100 percent relative humidity. H Film has a high degree of dimensional stability at elevated temperatures. Typical values for shrinkage are 0.3 percent at 200°C (392°F); 0.5 percent at 300°C (572°F); and 3.5 percent at 400°C (752°F).

For electrical insulation to be generally useful, it must perform its functions under a wide variety of atmospheric conditions and in environments containing solvents, oils, and other chemicals. H Film is insoluble in all common solvents with no change in physical properties after six months' immersion in hexane, benzene, dimethyl formamide, toluene, chloroform, methanol, chlorobenzene and acetone at room temperature and in hydrocarbon and chlorinated biphenyl transformer oils at 150°C. The hydrolytic stability of the film is very good with 75 percent of the elongation and 90 percent of the impact value being retained after 16 days in boiling water. In alkali and concentrated acid, however, H Film is subject to degradation. After exposure to air containing 2 percent ozone for 3700 hours, H Film still retains 50 percent of its elongation. Exposure to sunlight in Florida resulted in embrittlement of H Film in approximately six months, indicating a limit to its usefulness in applications requiring constant exposure to sunlight.

H Film has the best resistance to ionizing radiation of any other available organic film. After 10^8 roentgens (10^6 R/hour rate) exposure to gamma rays from a

Cobalt 60 source at Oak Ridge, there was no significant change in the mechanical or electrical properties of H Film. For the same exposure, Mylar retains less than 50 percent of its original tensile strength and elongation, while Teflon TFE retains less than 10 percent of its original values.

In summary, H Film possesses an outstanding combination of physical and electrical properties over a wide temperature range from cryogenic to Class H temperatures and above.